

Chapter: Covalent Bonds and Formulas

The Covalent Bond

Lesson Objectives

The student will:

- explain what covalent bonds are.
- explain why covalent bonds are formed.
- compare covalent bonds with ionic bonds in terms of how their definitions and how they are formed.
- draw Lewis structures for simple covalent molecules.
- use Lewis structures to show the formation of single, double, and triple covalent bonds.
- identify pairs of atoms that will form covalent bonds.
- define coordinate covalent bond.
- explain the equivalent bond strengths in resonance structures.

Vocabulary

- bond energy
- bond length
- coordinate covalent bond
- covalent bond
- double bond
- pi bond
- resonance
- sigma bond
- triple bond

Introduction

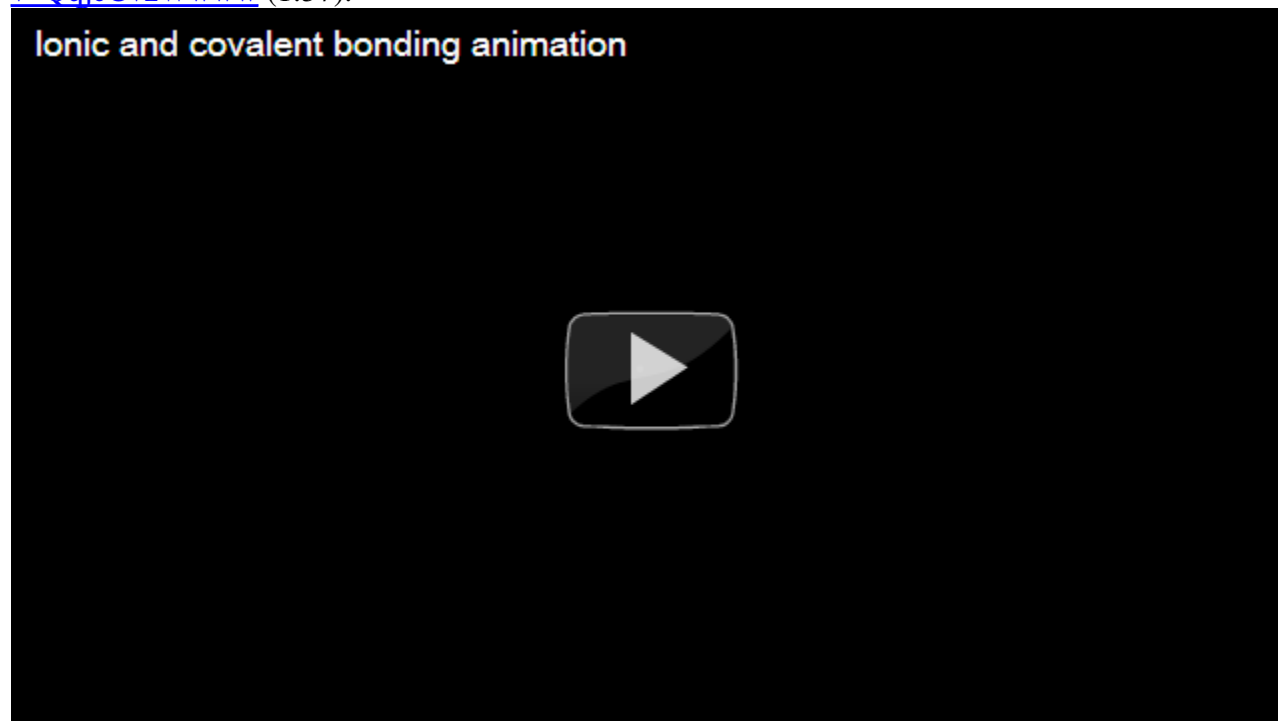
As we saw in the chapter “Ionic Bonds and Formulas,” metallic atoms can transfer one or more electrons to nonmetallic atoms, producing positively charged cations and negatively charged anions. The attractive force between these oppositely charged ions is called an ionic bond. However, chemical bonding does not require the complete transfer of electrons from one atom to another. When a bond forms between two nonmetallic atoms, neither has a low enough electronegativity to completely give up an electron to its partner. Instead, the atoms overlap their orbitals, and the electrons residing in these shared orbitals can be considered to be in the valence shells of both atoms at the same time. These atoms are now in a **covalent bond**, held together by the attraction of both nuclei to the shared electrons.

Ionic versus Covalent Bonding

The way that atoms bind together is due to a combination of factors: the electrical attraction and repulsion between atoms, the arrangement of electrons in atoms, and the natural tendency for matter to achieve the lowest potential energy possible. In most cases, these factors favor atoms that have obtained a complete octet of valence electrons. In ionic bonding, the atoms acquired this octet by gaining or losing electrons, while in covalent bonding, the atoms acquire the noble gas electron configuration by sharing electrons.

As you may recall from the discussion of ionic bonds in the chapter “Ionic Bonds and Formulas,” ionic bonds form between metals and nonmetals. Nonmetals, which have high electronegativity, are able to take electrons away from metals. The oppositely charged metal and nonmetal ions will then be attracted to each other. In covalent bonds, electrons are shared, meaning that metals will form few, if any, covalent bonds. Metals do not hold on to electrons with enough strength to participate in covalent bonding. For a covalent bond to form, we need two atoms that both attract electrons strongly, or two atoms with high electronegativity. Hence, the great majority of covalent bonds will form between two nonmetals. When both atoms in a bond are from the right side of the periodic table, the bond is most likely to be covalent.

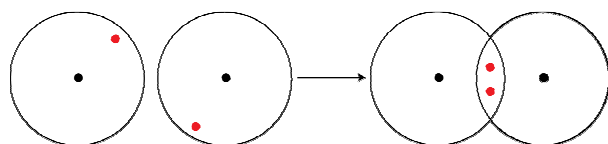
An animation showing ionic and covalent bonding (2a) is available at <http://www.youtube.com/watch?v=QqjCvzWwww> (1:57).



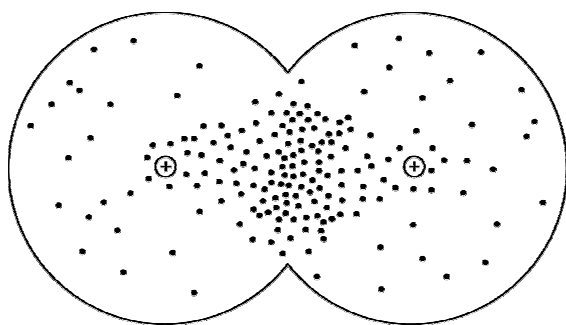
Single Bond

In covalent bonding, the atoms acquire a stable octet of electrons by sharing electrons. The covalent bonding process produces molecular substances, as opposed to the lattice structures produced by ionic bonding. The covalent bond, in general, is much stronger than the ionic bond, and there are far more covalently bonded substances than ionically bonded ones.

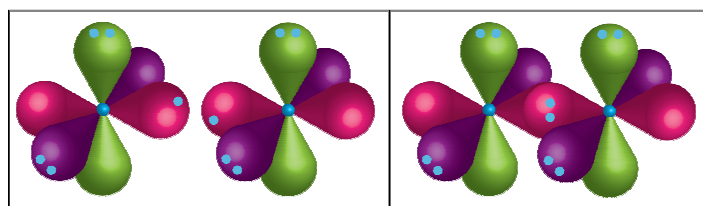
The simplest covalent bond is made between two atoms of hydrogen. Each hydrogen atom has one electron in its $1s$ orbital. When two hydrogen atoms approach one another and their orbitals overlap, it creates a common volume between the two nuclei that both electrons occupy (as seen in the figure below). Since these electrons are shared, both hydrogen atoms now have a full valence shell.



Since electrons are constantly in motion, they will not always be directly in the center of a covalent bond. However, the simulated probability pattern below shows that they do spend the majority of their time in the area directly between the two nuclei. The extra time spent between the two nuclei is the source of the attraction that holds the atoms together in a covalent bond.

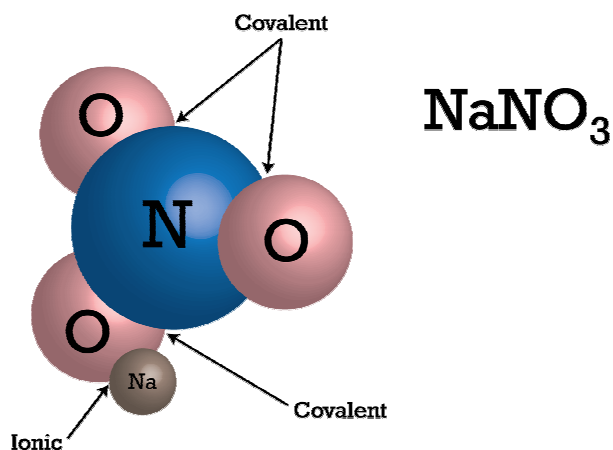


Another example of a covalent bond is found in the diatomic F_2 molecule (seen below). Recall that fluorine atoms have 7 valence electrons. Two are placed in the $2s$ orbital, and five are placed in the three $2p$ orbitals. Since each orbital can hold two electrons, this means that one of the $2p$ orbitals is only half full, so it is available for bonding. When two fluorine atoms interact, their half-filled orbitals overlap, creating a covalent bond that gives both atoms a complete octet of valence electrons.



Some Compounds Have Both Covalent and Ionic Bonds

If you recall the introduction to polyatomic ions, you will remember that the bonds that hold the polyatomic ions together are covalent bonds. Once the polyatomic ion is constructed with covalent bonds, it reacts with other substances as an ion. The bond between a polyatomic ion and another ion will be ionic. An example of this type of situation is in the compound sodium nitrate. Sodium nitrate is composed of a sodium ion and a nitrate ion. The nitrate ion is held together by covalent bonds, and the nitrate ion is attached to the sodium ion by an ionic bond (see sketch below).



Bond Strength

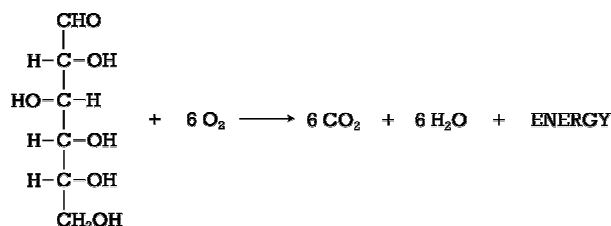
When atoms that attract each other move closer together, the potential energy of the system (the two atoms) decreases. When a covalent bond is formed, the atoms move so close together that their electron clouds overlap. As the atoms continue to move closer yet, the potential energy of the system continues to decrease – to a point. If you continue to move atoms closer and closer together, eventually the two nuclei will begin to repel each other. If you push the nuclei closer together beyond this point, the repulsion causes the potential energy to increase. Each pair of covalently bonding atoms will have a distance between their nuclei that is the lowest potential energy distance. This position has the atoms close enough for the attraction between the nucleus of one atom and the electrons of the other is maximum, but not too close that the nuclei have not begun to repel each other strongly. This distance is called the bond length. The more potential energy released as this bond formed, the stronger the bond will be. In order to break this bond, you must input an equivalent amount of energy.

The strength of a diatomic covalent bond can be expressed by the amount of energy necessary to break the bond and produce separate atoms. The energy needed to break a covalent bond is called **bond energy** and is measured in kilojoules per mole. Bond energy is used as a measure of bond strength. The bond strength of **HBr** is **365 kilojoules** per mole, meaning that it would take **365 kilojoules** to break all the chemical bonds in 1 mole, or 6.02×10^{23} molecules, of **HBr** and produce separate hydrogen and bromine atoms. In comparison, the bond strength of **HCl** is **431 kilojoules** per mole. Consequently, the bond in **HCl** is stronger than the bond in **HBr**.

Molecular Stability

The bond energy can be used to indicate molecular stability. When stable compounds are formed, large amounts of energy are given off. In order to break the molecule apart, all the energy that was given off must be put back in. The more energy needed to break a bond, the more stable the compound will be. Therefore, compounds with higher bond strengths tend to be more stable.

The molecule of glucose, shown below, can react with six molecules of oxygen to produce six molecules of carbon dioxide and six molecules of water. During the reaction, the atoms of the glucose molecule are rearranged into the structures of carbon dioxide and water. The bonds in glucose are broken, and new bonds are formed. As this occurs, potential energy is released because the new bonds have lower potential energy than the original bonds. Since the bonds in the products are lower energy bonds, the product molecules are more stable than the reactants.

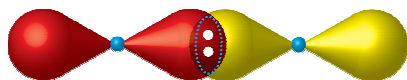


Double and Triple Bonds

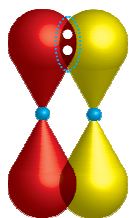
In the previous examples, only one pair of electrons was shared between the two bonded atoms. This type of bond is called a single bond. However, it is possible for atoms to share more than one pair of electrons. When two or three pairs of electrons are shared by two bonded atoms, they are referred to as **double bonds** or **triple bonds**, respectively.

A double bond is formed when two pairs of orbitals overlap with each other at the same time. The O_2 molecule provides an example of a double bond. Oxygen has six valence electrons. Two electrons are placed in the $2s$ orbital, while the remaining four are distributed among the three $2p$ orbitals. Hund's rule tells us that each p orbital will receive one electron before a second electron is added, so the oxygen atom will have two half-filled orbitals available for bonding (a filled orbital will not participate in bonding).

Of the two p orbitals available for bonding, the first pair will have a head-to-head overlap, placing the shared electrons directly in between the two nuclei. This type of a bond, shown in the figure below, is called a **sigma (σ) bond**.



The second pair of half-filled orbitals is orientated perpendicularly to the first pair, so a similar head-to-head overlap is not possible. However, a bond can still be made by overlapping the two p orbitals side-by-side, as shown in the figure below. This type of bond is called a **pi (π) bond**.



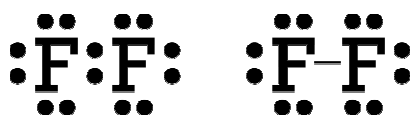
Whenever possible, the first bond will form directly between the two atomic nuclei involved in bonding. This allows for maximum overlap between the two orbitals, helping to minimize the electrostatic repulsion between the two positively charged nuclei. Thus, single bonds consist of one sigma bond, double bonds consist of one sigma and one pi bond, and triple bonds consist of one sigma and two pi bonds.

Note that double bonds are less than twice as strong as a single bond between the same two atoms. Since sigma bonds are “better” (stronger) than pi bonds, a combination of one sigma and one pi is slightly weaker than adding two sigma bonds together.

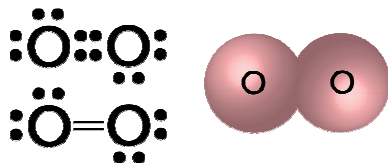
Lewis Dot Structures

It would not be very efficient if we had to draw an orbital picture every time we wanted to describe a molecule. Lewis dot structures, first developed by G.N. Lewis, are a shorthand way of drawing the arrangement of atoms, bonds, and valence electrons in a molecule. In the earlier chapter “The Electron Configuration of Atoms,” we introduced Lewis dot diagrams for drawing individual atoms. When we draw molecules, the diagrams are known as Lewis dot formulas, Lewis structures, or Lewis formulas. The Lewis structures of a molecule show how the valence electrons are arranged among the atoms of the molecule.

In a Lewis structure, each valence electron is represented by a dot, and bonds are shown by placing electrons in between the symbols for the two bonded atoms. Often, a pair of bonding electrons is further abbreviated by a dash. For example, we can represent the covalent bond in the F_2 molecule by either of the Lewis structures shown below.



Double bonds (4 electrons shared between two atoms) can be represented either with 4 dots or 2 dashes. The Lewis structure for an oxygen molecule (O_2) is shown below.

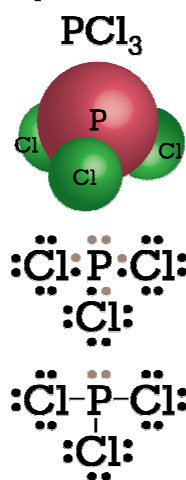


Similarly, triple bonds can be written as 6 dots or 3 dashes. An example of a molecule with triple bonds is the nitrogen molecule, N_2 . The Lewis structure for a nitrogen molecule can be represented by either of the two ways shown below. It is important to keep in mind that a dash always represents a pair of electrons. .

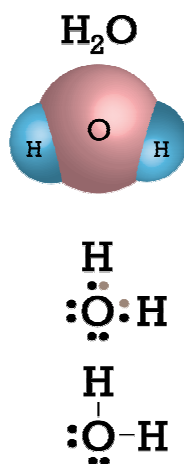


Several other examples of representing covalent bonds are shown in the figure below.

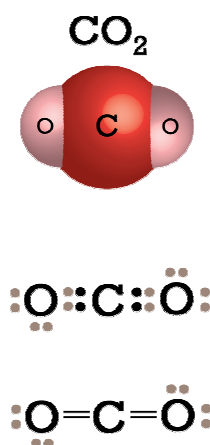
Phosphorus Trichloride



Water



Carbon Dioxide



Drawing Lewis Structures

The rules outlined below for writing Lewis structures are based on observations of thousands of molecules (note that there will be some exceptions to the rules). We learned earlier that atoms are generally most stable with 8 valence electrons (the octet rule). The major exception is hydrogen, which requires only 2 valence electrons to have a complete valence shell (sometimes called the duet rule). Lewis structures allow one to quickly assess whether each atom has a complete octet (or duet) of electrons.

Rules for Writing Lewis Structures:

1. Decide which atoms are bounded.
2. Count all the valence electrons of all the atoms.
3. Place two electrons between each pair of bounded atoms.
4. Complete all the octets (or duets) of the atoms attached to the central atom.
5. Place any remaining electrons on the central atom.
6. If the central atom does not have an octet, look for places to form double or triple bonds.

Example:

Write the Lewis structure for water, H_2O .

Step 1: Decide which atoms are bounded.

Begin by assuming the hydrogen atoms are bounded to the oxygen atom. In other words, assume the oxygen atom is the central atom.



Step 2: Count all the valence electrons of all the atoms.

The oxygen atom has 6 valence electrons, and each hydrogen has 1. The total number of valence electrons is 8.

Step 3: Place two electrons between each pair of bounded atoms.



Step 4: Complete all the octets or duets of the atoms attached to the central atom.

The hydrogen atoms are attached to the central atom and require a duet of electrons. Those duets are already present.

Step 5: Place any remaining electrons on the central atom.

The total number of valence electrons is 8, and we have already used 4 of them. The other 4 will fit around the central oxygen atom.



Is this structure correct?

- Are the total number of valence electrons correct? Yes
- Does each atom have the appropriate duet or octet of electrons? Yes

The structure, then, is correct.

Example:

Write the Lewis structure for carbon dioxide, CO_2 .

Step 1: Decide which atoms are bounded.

Begin by assuming the carbon is the central atom and that both oxygen atoms are attached to the carbon.

Step 2: Count all the valence electrons of all the atoms.

The oxygen atoms each have 6 valence electrons and the carbon atom has 4. The total number of valence electrons is 16.

Step 3: Place two electrons between each pair of bounded atoms.



Step 4: Complete all the octets or duets of the atoms attached to the central atom.



Step 5: Place any remaining electrons on the central atom.

We have used all 16 of the valence electrons so there are no more to place around the central carbon atom.

Is this structure correct?

- Is the total number of valence electrons correct? Yes
- Does each atom have the appropriate duet or octet of electrons? NO

Each oxygen has the proper octet of electrons, but the carbon atom only has 4 electrons. Therefore, this structure is *not* correct.

Step 6: If the central atom does not have an octet, look for places to form double or triple bonds.

Double bonds can be formed between carbon and each oxygen atom.



Notice this time that each atom is surrounded by 8 electrons.

Example:

Write the Lewis structure for ammonia, NH_3 .

Step 1: Decide which atoms are bounded.

The most likely bonding for this molecule is to have nitrogen as the central atom and each hydrogen

bounded to the nitrogen. Therefore, we can start by putting nitrogen in the center and placing the three hydrogen atoms around it.

Step 2: Count all the valence electrons of all the atoms.

The nitrogen atom has five valence electrons, and each hydrogen atom has one. The total number of valence electrons is 8.

Step 3: Place two electrons between each pair of bounded atoms, as seen in the middle drawing of the figure below.



Step 4: Complete all the octets or duets of the atoms attached to the central atom.

In this case, all the non-central atoms are hydrogen, and they already have a duet of electrons.

Step 5: Place any remaining electrons on the central atom.

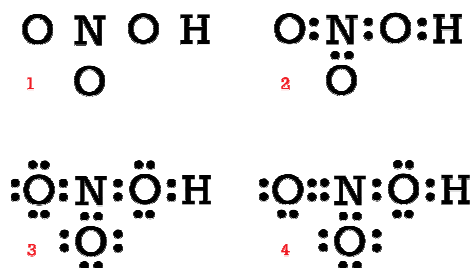
There are still two electrons left, so they would complete the octet for nitrogen. If the central atom, at this point, does not have an octet of electrons, we would look for places to create a double or triple bond, but that is not the case here. The final drawing on the right in the figure above is the Lewis structure for ammonia.

Example:

Write the Lewis structure for nitric acid, HNO_3 .

Solution:

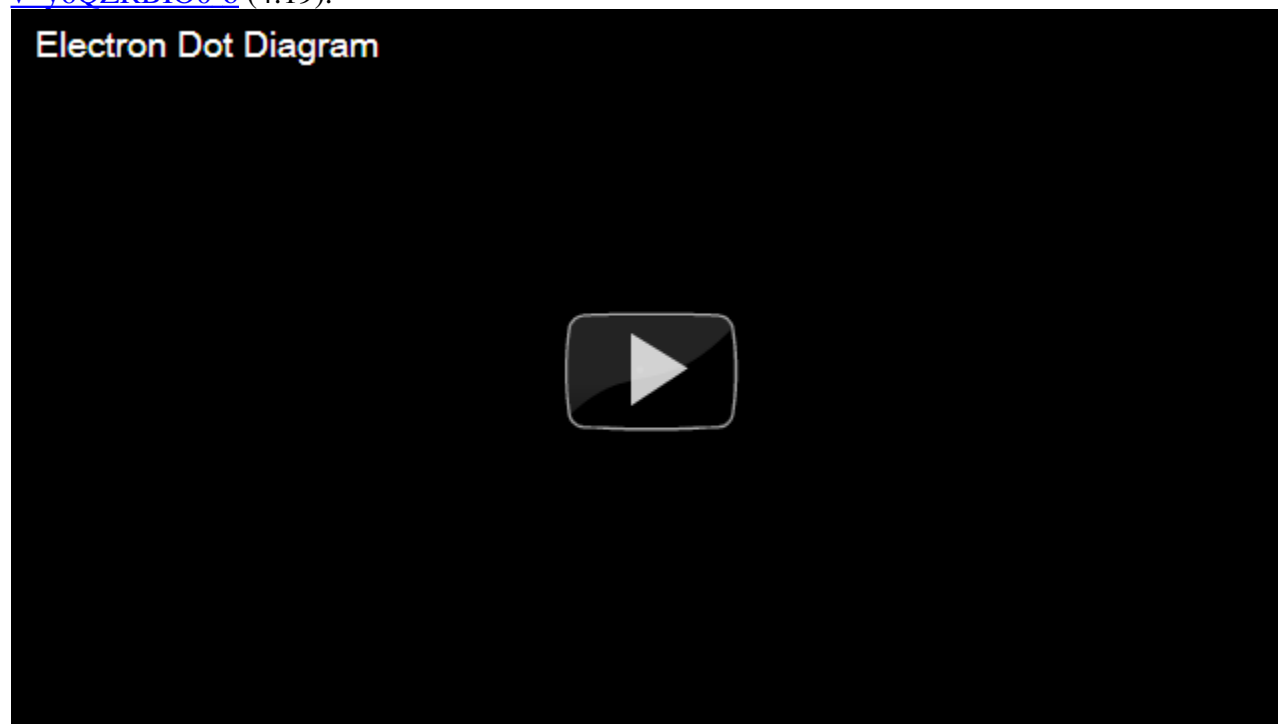
The skeleton for nitric acid has the three oxygen atoms bounded to the nitrogen and the hydrogen bounded to one of the oxygen atoms, as seen in diagram 1 shown below. The total number of valence electrons is $5 + 6 + 6 + 6 + 1 = 24$.



The next step, shown in diagram 2, is to put in a pair of electrons between each bonded pair. So far, we have accounted for 8 of the 24 valence electrons. The next step is to complete the octet or duet for each of the non-central atoms, as seen in diagram 3. At that point, we have used all of the valence electrons, but the central atom does not have an octet of electrons. The rules tell us to find a place to put a double or triple bond. Based on what we have learned up to this point, any of the three oxygen atoms is just as good as the others for participating in a double bond. For this example, we moved two of the electrons

from the oxygen atom on the far left between the oxygen and nitrogen. Now every atom in the molecule has the appropriate octet or duet of electrons. We have a satisfactory Lewis structure for the nitric acid molecule.

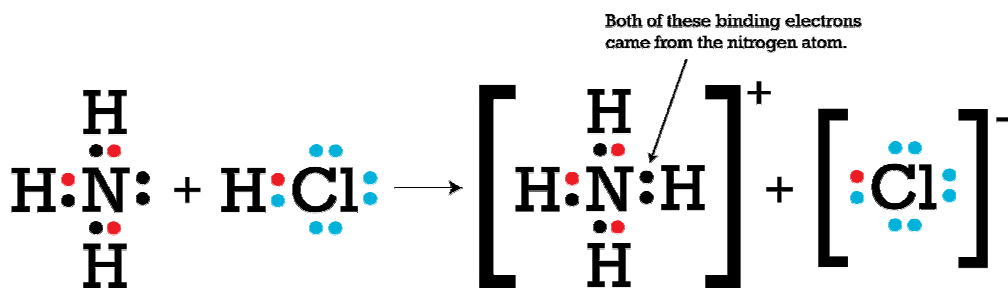
For an introduction to drawing Lewis electron dot symbols (2e), see <http://www.youtube.com/watch?v=y6QZRBIO0-o> (4:19).



Coordinate Covalent Bond

A variation of covalent bonding is coordinate covalent bonding. **Coordinate covalent bonds** form when the two shared electrons of a covalent bond are both donated by the same atom. So far, we have looked at covalent bonds formed by the overlap of two half-filled orbitals. A coordinate covalent bond is different in that it involves the overlap of one full orbital and one empty one. Once formed, a coordinate covalent bond is no different from an ordinary covalent bond. The difference is simply in the source of the electrons forming the bond. You should note that the bond still involves only one pair of electrons and one pair of orbitals, but only one atom provides both of the shared electrons. Many polyatomic ions include coordinate covalent bonds. The ammonium ion is an example of this type of bonding. When hydrogen chloride gas and ammonia gas are brought into contact with each other, they form ammonium chloride, NH_4Cl . When ammonium chloride is dissolved in water, ammonium ions and chloride ions are produced.





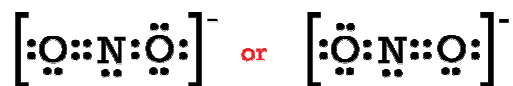
In one of the nitrogen-hydrogen bonds, both electrons came from the nitrogen atom. However, once the ammonium ion has been formed, all four nitrogen-hydrogen bonds are identical, regardless of where the electrons in the bonds came from.

Resonance

Sometimes, more than one valid Lewis structure is possible for the same molecule. Consider the Lewis structure for the nitrite ion, NO_2^- . The charge on the ion indicates an electron has been gained from an external source. In other words, the ion contains an electron that did not originally belong to the nitrogen or the oxygen atoms in the ion. In this case, the -1 charge indicates that the valence electron count will have one additional electron added in order to account for the electron that came from outside the ion. The total number of valence electrons for this ion is $5 + 6 + 6 + 1 = 18$. We can then draw the Lewis structure for this ion following the normal rules. Before applying the last rule of creating double or triple bonds, the incomplete Lewis structure will look like that in the figure below.

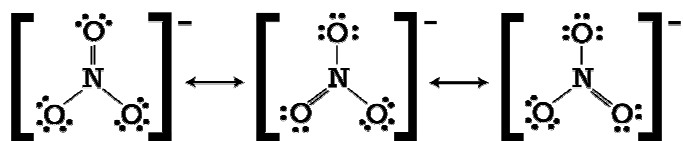


All 18 of the available valence electrons have been used. The final rule for writing Lewis structures states that if the central atom does not have an octet of electrons, double or triple bonds need to be created. In this case, either one of the nitrogen-oxygen bonds can be made into a double bond, as demonstrated in the figure below.



The two structures in the image above suggest that one of the nitrogen-oxygen bonds should be shorter and stronger than the other one. It has been experimentally shown, however, that the two nitrogen-oxygen bonds are identical. In fact, the nitrogen-oxygen bond lengths are about halfway between the expected values for a single bond and a double bond. Neither of the Lewis structures above matches the experimental evidence, and there is no good way to write one that does. The solution to this problem is the use of a concept called **resonance**. Resonance is the condition where there is more than one valid Lewis structure can be written for the molecule or ion. The actual structure of the molecule or ion is actually a composite, or average, of all the valid Lewis structures. In the case of the nitrite ion above, the second pair of electrons in the double bond is actually shared between all the atoms, giving each bond the strength of about 1.5 bonds. Each of the Lewis structures that is drawn is called a resonance structure, with the actual structure being a resonance hybrid of all the contributing structures.

Resonance is also present in the Lewis structures for nitrate ion, NO_3^- .



All of these are valid Lewis structures, but none of them accurately portray the structure of the ion. Just like in the case of nitrite, the actual nitrate ion is an average of all three structures. All three nitrogen-oxygen bonds are identical, and they are all slightly shorter and stronger than a normal nitrogen-oxygen single bond. We saw earlier that the second bond in a double bond is a pi bond, created by two *p* orbitals lining up side by side. It is those pi electrons that cannot be described well by a single Lewis structure. Rather than creating a true pi bond between just two atoms, the extra electrons are shared among all four atoms.

When the concept of resonance was first introduced, it was thought that the molecule was rapidly switching, or resonating, between the various resonance forms. Although later evidence showed that this is not the case, the term has survived. Note the double headed arrows (\longleftrightarrow) between each structure. Using this type of arrow indicates that the structures shown are resonance structures, implying that the entire figure attempts to describe a single molecule or ion.

Lesson Summary

- Covalent bonds are formed by electrons being shared between two atoms.
- Covalent bonds are formed between atoms with relatively high electronegativity.
- Bond energy is the amount of energy necessary to break the covalent bond and is an indication of the strength and stability of the bond.
- Some atoms are capable of forming double or triple bonds.
- Multiple bonds between atoms require multiple half-filled orbitals.
- End-to-end orbital overlaps are called sigma bonds.
- Side-to-side orbital overlaps are called pi bonds.
- Lewis structures are commonly used to show the valence electron arrangement in covalently bonded molecules.
- Resonance is a condition occurring when more than one valid Lewis structure can be written for a particular molecule. The actual electronic structure is not represented by any one of the Lewis structures but by the average of all of the valid structures.

Further Reading / Supplemental Links

The learner.org website allows users to view the Annenberg series of chemistry videos. You are required to register before you can watch the videos, but there is no charge to register. The video called “Chemical Bonds” explains the differences between ionic and covalent bonds using models and examples from nature.

- http://www.learner.org/vod/vod_window.html?pid=800

This animation explores the differences between ionic and covalent bonding.

- http://www.mhhe.com/physsci/chemistry/animations/chang_7e_esp/bom1s2_11.swf

This website provides more information about the different types of chemical bonding.

- http://www.visionlearning.com/library/module_viewer.php?mid=55

The website below provides a guide to drawing Lewis structures.

- <http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch8/lewis.html#step>

Review Questions

1. Describe the characteristics of two atoms that would be expected to form an ionic bond.
2. Describe the characteristics of two atoms that would be expected to form a covalent bond.
3. If a molecule had a very high bond energy, would you expect it to be stable or unstable?
4. When gaseous potassium ions and gaseous fluoride ions join together to form a crystal lattice, the amount of energy released is **821 kJ/mol**. When gaseous potassium ions and gaseous chloride ions join together to form a crystal lattice, the amount of energy released is **715 kJ/mol**. Which bond is stronger, **KF** or **KCl**? If these two compounds were increasingly heated, which compound would break apart at the lower temperature?
5. Of the following compounds listed in **Table below**, which would you expect to be ionically bonded and which would you expect to be covalently bonded?

Table for Review Question 5

Compound Ionic or Covalent

CS₂

K₂S

FeF₃

PF₃

BF₃

AlF₃

BaS

6. How many sigma bonds and how many pi bonds are present in a triple bond?
7. Which of the following molecules will have a triple bond?
 1. **C₂H₂**
 2. **CH₂Cl₂**
 3. **BF₃**
 4. **CH₃CH₂OH**
 5. **HF**
8. Draw the Lewis structure for **CCl₄**.
9. Draw the Lewis structure for **SO₂**.
10. Draw a Lewis structure for **CO₃²⁻**. Explain why all three carbon-oxygen bonds have the same length.

Covalent Formulas and Nomenclature

Lesson Objectives

The student will:

- list the Greek prefixes from 1 to 10.

- provide the correct formulas for binary covalent compounds.
- name binary covalent compounds using the IUPAC nomenclature system.

Vocabulary

- chemical nomenclature

Introduction

The systematic procedure for naming chemical compounds, or the **chemical nomenclature**, is different for different types of compounds. In the chapter “Ionic Bonds and Formulas,” we have discussed the procedures for naming binary ionic compounds, ionic compounds involving polyatomic ions, and ionic compounds involving metals with variable oxidation states. In this section, we will describe chemical nomenclature for covalently bonded compounds. Because of the large numbers of covalent compounds that may form between the same two elements, the nomenclature system for covalent compounds is somewhat different to the nomenclature system for ionic compounds.

In naming ionic compounds, there is no need to indicate the number of atoms of each element in a formula because, for most cases, there is only one possible compound that can form from the ions present. When aluminum combines with sulfur, the only possible compound is aluminum sulfide, Al_2S_3 . The only exception to this is a few metals with variable oxidation numbers, and these are handled by indicating the oxidation number of the metal with Roman numerals, such as in iron(II) chloride, FeCl_2 .

With covalent compounds, however, we have a very different situation. There are six different covalent compounds that can form between nitrogen and oxygen, and for two of them, nitrogen has the same oxidation number. Therefore, the Roman numeral system will not work. Instead, chemists devised a nomenclature system for covalent compounds that would indicate how many atoms of each element is present in a molecule of the compound.

Greek Prefixes

In naming binary covalent compounds, four rules apply:

1. The first element in the formula is named first using the normal name of the element.
2. The second element is named as if it were an anion. There are no ions in these compounds, but we use the “-ide” ending on the second element as if it were an anion.
3. Greek prefixes, shown in **Table below**, are used for each element to indicate the number of atoms of that element present in the compound.
4. The prefix “mono-” is never used for naming the first element. For example, CO is called carbon monoxide, *not* monocarbon monoxide.

Greek Prefixes

Prefix	Number Indicated
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Mono-	1
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Di-	2
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Tri-	3
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Tetra-	4
--------	---

Penta-	5
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Hexa- 6
Hepta- 7
Octa- 8
Nona- 9
Deca- 10

Examples:

N_2O dinitrogen monoxide
 NO nitrogen monoxide
 NO_2 nitrogen dioxide
 N_2O_3 dinitrogen trioxide
 N_2O_4 dinitrogen tetroxide
 N_2O_5 dinitrogen pentoxide
 SF_6 sulfur hexafluoride
 CO_2 carbon dioxide
 P_4O_{10} tetraphosphorus decaoxide
 P_2S_5 diphosphorus pentasulfide

Lesson Summary

- Covalently bonded molecules use Greek prefixes in their nomenclature.

Further Reading / Supplemental Links

This website reviews the rules for naming binary covalent compounds and includes a quiz to test your understanding of these rules.

- http://www.chem.purdue.edu/gchelp/nomenclature/covalent_2009.htm

Review Questions

- Name the compound CO .
- Name the compound PCl_3 .
- Name the compound PCl_5 .
- Name the compound N_2O_3 .
- Name the compound BCl_3 .
- Name the compound SF_4 .
- Name the compound Cl_2O .
- Write the formula for the compound sulfur trioxide.
- Write the formula for the compound dinitrogen tetrafluoride.
- Write the formula for the compound oxygen difluoride.
- Write the formula for the compound dinitrogen pentoxide.
- Write the formula for the compound sulfur hexafluoride.
- Write the formula for the compound tetraphosphorus decaoxide.

Electronic and Molecular Geometry

Lesson Objectives

The student will:

- identify the most likely type of bonding (ionic, covalent, or polar covalent) for each compound given binary formulas and an electronegativity chart.
- draw Lewis structures for simple molecules that violate the octet rule.
- from a list of binary compounds, identify those that require electron promotion in the explanation of their bonding.
- identify the type of hybridization in various molecules.
- explain the necessity for the concept of hybridized orbitals.

Vocabulary

- electron promotion
- orbital hybridization
- polar covalent bonds

Introduction

In your study of chemistry, you may have noticed occasionally that after you have learned the “rules” for how matter behaves, you are introduced to the exceptions. For example, shortly after you learned the filling order rule for electron configuration, you were introduced to the exceptions caused by the slightly lower potential energy when the *d* orbitals were exactly half-filled or completely filled. Shortly after you learned that metals lose all their valence electrons when forming ions, you were introduced to some variable oxidation number metals that give up a different number of electrons.

In this section, you will be introduced to exceptions to the octet rule. Most of the exceptions to rules in chemistry are due to the fact that the behavior of matter is controlled by the tendency toward lowest potential energy. Therefore, when a small variation to the rule produces slightly lower potential energy, matter will follow that path.

Electronegativity

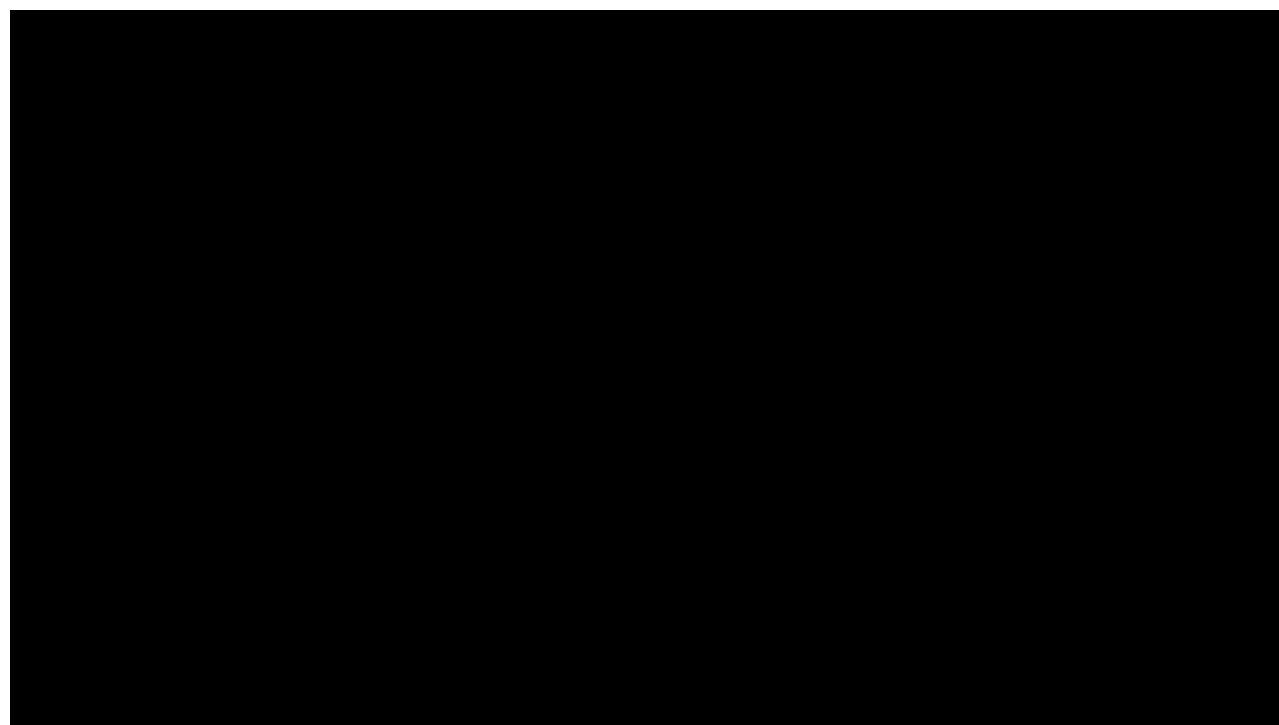
Recall from the chapter on “Chemical Periodicity” that the ability for an atom in a molecule to attract shared electrons is called electronegativity. The electronegativity of atoms has been quantified in several ways. One method that is widely accepted is that of Linus Pauling. The Pauling electronegativity values are shown below.

1 H 2.20																
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98
11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16
19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96
37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66
55 Cs 0.79	56 Ba 0.89	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Tl 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2
87 Fr 0.7	88 Ra 0.9															

When two atoms combine, the difference between their electronegativities is an indication of the type of bond that will form. If the difference between the electronegativities of the two atoms is small, neither atom can take the shared electrons completely away from the other atom, and the resulting bond will be covalent. If the difference between the electronegativities is large, the more electronegative atom will take the bonding electrons completely away from the other atom (electron transfer will occur), and the bond will be ionic. There is no exact number for the difference in electronegativity that will produce an ionic bond, but many chemists suggest **1.7** as the approximate difference that will produce an ionic bond.

If we compare a few electronegativities, we can see that **1.7** is a reasonable suggestion. The difference between the electronegativities of hydrogen and oxygen is **1.2**, and we know the bonds in the water molecule are covalent. In magnesium chloride, the electronegativity difference is **1.8**, and we know this molecule contains ionic bonds.

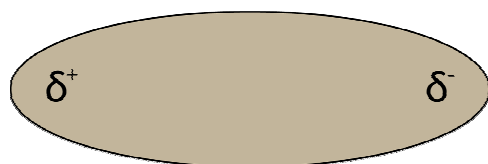
This video describes ionic, covalent, and polar covalent bonds and relates the types of bonds formed to the differences in electronegativity of the bonding atoms (2g): <http://www.youtube.com/watch?v=tSG4R4YZUW8> (5:17).



The Partial Ionic Character of Covalent Bonds

So far, we have discussed two extreme types of bonds. One case is when two identical atoms bond. They have exactly the same electronegativities, thus the two bonded atoms pull exactly equally on the shared electrons. The other case is when the bonded atoms have a very large difference in their electronegativities. In this case, the more electronegative atom will take the electrons completely away from the other atom, forming an ionic bond.

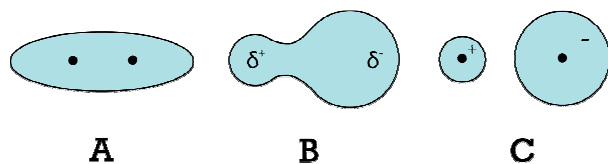
What about the molecules whose electronegativities are not the same but the difference is not as large as 1.7? For these molecules, the electrons are still shared by the two atoms, but they are not shared equally. The shared electrons are pulled closer to the more electronegative atom. This results in an uneven distribution of electrons over the molecule and causes slight charges on opposite ends of the molecule. Such molecules are said to have a dipole or are called polar molecules (see figure below). These charges are not full $+1$ and -1 charges, but rather they are fractions of charges. For small fractions of charges, we use the symbols $\delta+$ and $\delta-$.



Atoms whose electronegativities are not the same but are not different enough to cause complete electron transfer will form **polar covalent bonds**. These polar covalent bonds will be discussed in more detail later on in this chapter. With the introduction of the polar covalent bond, we now know of three different types of bonds.

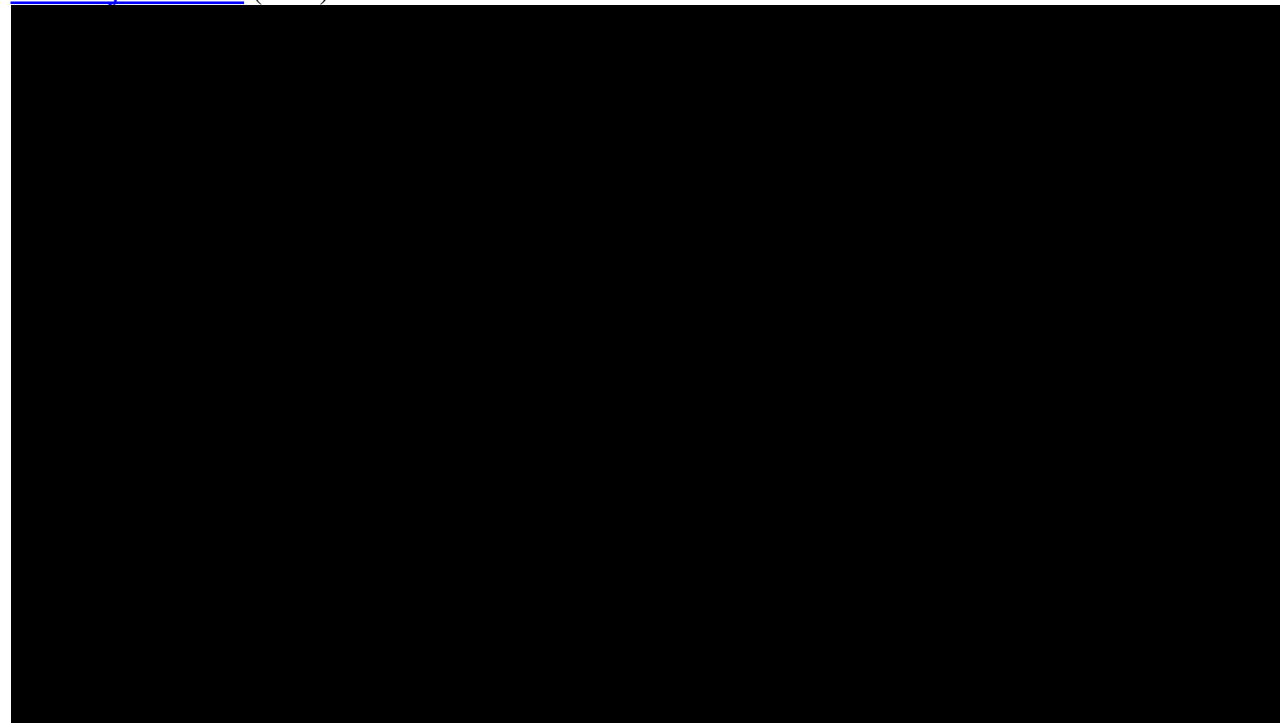
In the figure below, molecule A represents a perfectly covalent bond that would form between identical atoms. Molecule B is a polar covalent bond formed between atoms whose electronegativities are not the same but whose electronegativity difference is less than 1.7, while molecule C is an ionic bond formed

between atoms whose electronegativity difference is greater than 1.7.



For an introduction to polar bonds see these two videos. The first video defines polar bonds. The second one consists of lecture and animation about polar bonds and polar molecules (**2b**, **2f**):

<http://www.youtube.com/watch?v=rRoLSBeOjME> (1:49), <http://www.youtube.com/watch?v=LKAjTE7B2x0> (4:43).



Polar bond



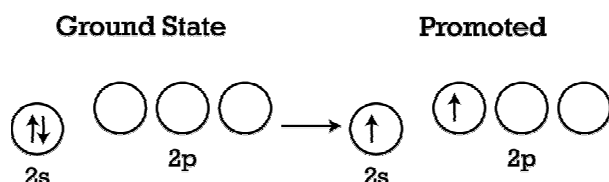
Electron Promotion

Consider the molecule formed by the combination of beryllium and hydrogen, beryllium hydride (BeH_2). The electronegativity difference between these two atoms is only **0.6**, with beryllium being slightly more electropositive. Therefore, the bonds in BeH_2 are polar covalent bonds. The Lewis structure for the molecule is:



The first thing we might notice about the BeH_2 molecule is that it does not obey the octet rule. Beryllium has two valence electrons and each hydrogen has one, so there are not enough valence electrons to produce an octet around the beryllium atom.

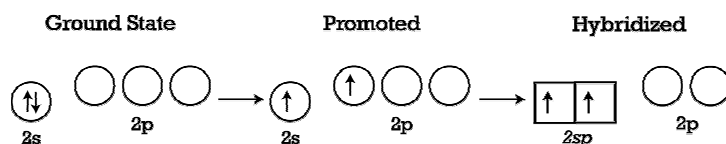
There is also another unusual thing about BeH_2 . The orbital representation for the electron configuration of beryllium shows the **2s** orbital is full. Earlier in this chapter, we said that the atoms involved in covalent bonding must each have a half-filled orbital. How can beryllium form two bonds when it does not have any half-filled orbitals? The explanation to this question involves the concept of **electron promotion**. As illustrated below, by promoting an electron from the **2s** orbital to one of the **2p** orbitals, beryllium theoretically acquires two half-filled orbitals. These half-filled orbitals are therefore able to form two covalent bonds. The amount of necessary to promote an electron from a **2s** orbital to a **2p** orbital is small compared to the amount of energy released when beryllium forms two covalent bonds. As a result, in exchange for a small input of energy, a large quantity of energy released.



Orbital Hybridization

We have not, however, completed the explanation as to why BeH_2 does not follow the octet rule. Bonds formed by overlapping s orbitals are, in general, shorter, stronger, and more flexible than bonds formed by overlapping p orbitals from the same shell. Therefore, when considering the two bonds in BeH_2 , it would be reasonable to assume that we could determine which bond was formed by hydrogen overlapping with beryllium's half-filled $2s$ orbital and which was formed by hydrogen overlapping beryllium's half-filled $2p$ orbital. Examination of the two bonds, however, shows them to be identical in length, strength, and flexibility. The values for the length, strength, and flexibility also fall in between the values expected for overlapping s and p orbitals. The concept used to explain these observations is called **orbital hybridization**.

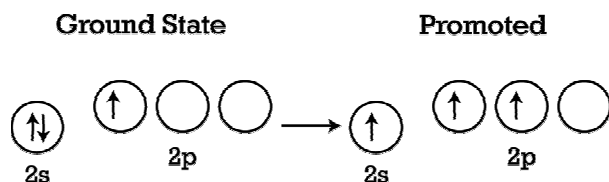
In orbital hybridization, all the orbitals involved in bonding are hybridized and form a set of identical orbitals that have properties intermediate to the properties of the orbitals from which they were created.



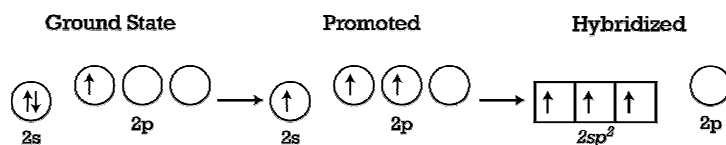
As seen in the image above, the half-filled $2s$ and $2p$ orbitals hybridize to form two completely new orbitals named sp hybridized orbitals. These two new orbitals are identical to each other, and both have characteristics somewhere between the characteristics of $2s$ and $2p$ orbitals. When these half-filled sp hybridized orbitals overlap with the hydrogen atoms, two identical bonds are produced.

Covalent Bonds of Group 3A

The only member of Group 3A that forms a significant number of covalent compounds is boron. Numerous boron compounds exist, with boron forming three bonds in many of the compounds. Since the ground state electron configuration of boron, $1s^2 2s^2 2p^1$, has a filled $2s$ orbital and one half-filled $2p$ orbital, the concept of electron promotion is needed to explain boron's formation of three bonds.



One of the electrons in the $2s$ orbital is promoted to an empty $2p$ orbital, producing three half-filled orbitals that allows boron to form three covalent bonds (illustrated in the figure above). The three bonds in boron compounds such as BH_3 are found to be identical in length, strength, and flexibility. The $2s$ orbital and two $2p$ orbitals hybridize to form three identical sp^2 hybridized orbitals.

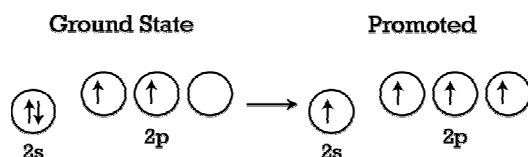


The three hybridized orbitals can now overlap with other atoms and form three identical bonds, making compounds such as BH_3 and BCl_3 . In these boron compounds, the central atom is surrounded by only six electrons, and therefore this is another exception to the octet rule.

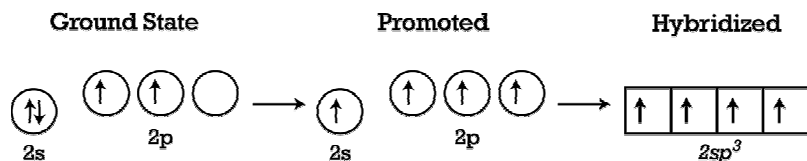
It should be recognized that the sp^2 hybridized orbitals are not the same as sp hybridized orbitals. If you mix one bucket of blue paint with one bucket of yellow paint, you get green paint. If you mix two buckets of blue with one bucket of yellow, you will also get green paint, but it will not be the same shade of green as before. Hybridizing one s and one p orbital does not produce the same orbitals as hybridizing one s and two p orbitals.

Covalent Bonds of Group 4A

The members of Group 4A that form covalent bonds are carbon and silicon. Their electron configurations are $1s^2 2s^2 2p^2$ and $1s^2 2s^2 2p^6 3s^2 3p^2$, respectively. In the outer energy level of both atoms, the s orbital is filled, two of the p orbitals are half-filled, and the third p orbital is empty. In the majority of the covalent compounds containing carbon and silicon, these atoms are found to have four bonds. As a result, electron promotion must also occur in these atoms. If one of the electrons in the s orbital is promoted to the empty p orbital, four half-filled orbitals are produced, as shown in the image below.



With four half-filled orbitals, carbon and silicon can form the four covalent bonds necessary to create CH_4 , CCl_4 , and so on. As you may have already suspected, the four bonds in carbon and silicon compounds are all identical. Therefore, orbital hybridization also occurs in this family. The four hybridized orbitals, as shown below, are called sp^3 hybridized orbitals.

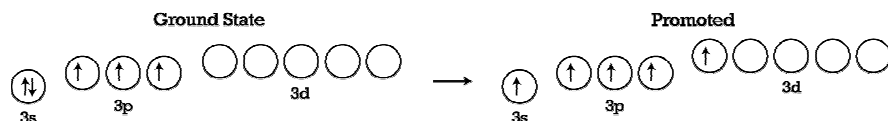


Since the sp^3 hybridized orbitals are a mix of one s and three p orbitals, their characteristics are not the same as sp^2 hybridized orbitals or sp hybridized orbitals. These four identical orbitals can be overlapped by four hydrogen atoms and form four identical bonds. Consequently, the covalent compounds in Group 4A do obey the octet rule.

Covalent Bonds of Group 5A

In Group 5A, the electron configuration of the outermost energy level is $s^2 p^3$. These atoms have three

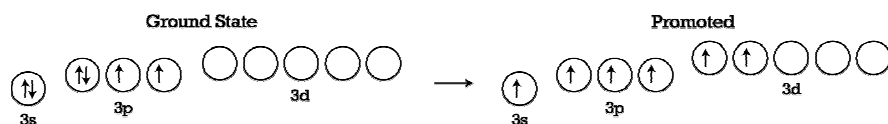
half-filled *p* orbitals available for bonding and would appear to form three covalent bonds with no need for either electron promotion or hybridization. The first member of the family, nitrogen, commonly forms three bonds in compounds such as NH_3 , NCl_3 , and N_2O_3 . The second member of the family, phosphorus, also forms similar compounds, like PH_3 and PCl_3 . Phosphorus, however, can also form compounds with five covalent bonds, such as PCl_5 . In order to explain five identical bonds for the phosphorus atom, we will need to use the concepts of electron promotion and orbital hybridization.



As shown in the figure above, phosphorus promotes one of its 3s electrons into an orbital in the 3d sub-level. This gives phosphorus five half-filled orbitals and allows it to form the five bonds in PCl_5 and other phosphorus compounds with five covalent bonds. It also makes it clear why nitrogen does not form compounds with five bonds, because nitrogen does not have a *d* sub-energy level available. The five bonds in these compounds are identical, which means that one *s* orbital, three *p* orbitals, and one *d* orbital hybridize. These hybridized orbitals will be called sp^3d or dsp^3 hybridized orbitals. Molecules like PCl_5 and PF_5 will have the central atom surrounded by 10 electrons, so this electron promotion produces another group of molecules that do not obey the octet rule.

Covalent Bonds of Group 6A

The outermost energy level of the members of Group 6A has the electron configuration s^2p^4 . This outer energy level has a filled *s* orbital, one filled *p* orbital, and two half-filled *p* orbitals. With two half-filled orbitals available for overlap, all of the members of this family can and do form two covalent bonds. There are, however, some compounds that form more than two covalent bonds. Oxygen has no *d* orbitals, so promotion into the *d* sub-energy level is not possible. Sulfur and larger members of the family, however, do have *d* orbitals that allow for electron promotion.



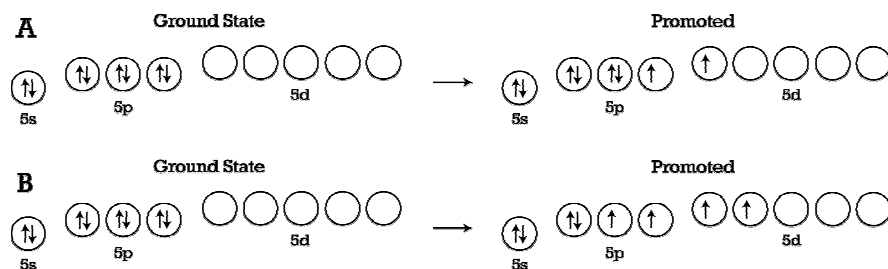
As you can see in the image above, sulfur can promote two electrons into the *d* orbitals and produce six half-filled orbitals available for overlap. The six orbitals are hybridized and form d^2sp^3 or sp^3d^2 hybridized orbitals. Such orbitals are necessary for the formation of compounds such as SF_6 .

Covalent Bonds of Group 7A

All of the members of Group 7A have outermost energy level electron configurations s^2p^5 . This configuration has one half-filled *p* orbital, which allows the members of this family to form one covalent bond. The majority of compounds formed by this family contain one bond. Fluorine has no *d* orbitals and can only form one bond. Unlike fluorine, chlorine and the larger members of the family have empty *d* orbitals that allow them to undergo electron promotion. Chlorine can promote one *p* electron to a *d* orbital to produce three half-filled orbitals, which allow compounds like ClF_3 to form. Chlorine can also promote two electrons to form five half-filled orbitals, which results in compounds like ClF_5 .

Covalent Bonds of Group 8A

Even members of the noble gases, under extreme conditions, can form some covalent compounds. Since the ground state electron configuration for these atoms has completely filled outer energy levels, the only way that they can form bonds is by electron promotion and orbital hybridization.



In the diagram above, figure A shows xenon promoting one electron from a *p* to a *d* orbital. This allows xenon to form compounds like XeF_2 that contain two covalent bonds. In figure B, xenon is promoting two electrons from *p* to *d* orbitals, producing four orbitals available for bonding and forming compounds like XeF_4 . In both Groups 7A and 8A, when electrons are promoted and orbitals are hybridized, even though some of the orbitals are filled and some are half-filled, hybridization is considered to involve *all* the outer energy level orbitals that contain electrons. Therefore, in figure A, the orbital hybridization would be sp^3d , and in figure B, the hybridization would be sp^3d^2 .

Table [below](#) summarizes the different types of hybridized orbitals discussed in this section.

Summary of Hybridized Orbitals

Orbitals Hybridized	Hybridized Orbital Names	Number of Orbitals
$s + p$	sp	2
$s + p + p$	sp^2	3
$s + p + p + p$	sp^3	4
$s + p + p + p + d$	sp^3d	5
$s + p + p + p + d + d$	sp^3d^2	6

This animation reviews the differences in ionic, covalent, and polar covalent bonds (**2a**): <http://www.youtube.com/watch?v=Kj3o0XvhVqQ> (1:26).

Electronegativity



Lesson Summary

- A difference of approximately 1.7 or more in the electronegativities of bonded atoms will produce an ionic bond.
- Bonds between atoms whose electronegativity difference is between 0 and 1.7 will be polar covalent.
- A relatively small number of stable molecules do not obey the octet rule.
- Electron promotion occurs within an energy level when an electron from a lower sub-energy level is promoted to a higher sub-energy level.
- The concept involved in orbital hybridization is that all the orbitals of an atom that are involved in bonding are hybridized to orbitals that are identical and have properties intermediate to the properties of the orbitals that are hybridized.
- Covalent bonding in Group 2A involves electron promotion and sp hybridization.
- Covalent bonding in Group 3A involves electron promotion and sp^2 hybridization.
- Covalent bonding in Group 4A involves electron promotion and sp^3 hybridization.
- Covalent bonding in Group 5A involves electron promotion and sp^3d hybridization.
- Covalent bonding in Group 6A involves electron promotion and sp^3d^2 hybridization.
- Covalent bonding in Group 8A involves electron promotion and can involve sp^3d or sp^3d^2 hybridization.

Further Reading / Supplemental Links

The following websites provide more information on electron promotion and orbital hybridization.

- <http://www.mikeblaber.org/oldwine/chm1045/notes/Geometry/Hybrid/Geom05.htm>
- <http://pages.towson.edu/ladon/carbon.html>

This video is a ChemStudy film called “Shapes and Polarities of Molecules.”

- <http://www.youtube.com/watch?v=BnU2idxQ3Xc>

Review Questions

1. Explain the differences among a covalent bond, a polar covalent bond, and an ionic bond.
2. Explain why a pair of atoms form a covalent bond rather than an ionic bond.
3. Predict which of the following bonds will be more polar and explain why: $\text{P} - \text{Cl}$ or $\text{S} - \text{Cl}$.
4. What laboratory evidence necessitates the theory of hybridized orbitals?
5. Which of the following molecules has a central atom with sp^2 hybridized orbitals?
 1. C_2H_2
 2. CH_2Cl_2
 3. BF_3
 4. $\text{CH}_3\text{CH}_2\text{OH}$
 5. HF
6. Fill in the type of hybridization necessary for the following molecules in **Table below**.

Table for Review Question 6

Molecule Type of Hybridization

H_2O

NH_3

BeCl_2

NaH

BF_3

PCl_5

BrF_5

SF_6

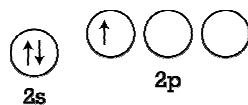
XeF_2

Answer questions 7-10 by following the example below.

Example: The formula for boron trichloride is BCl_3 .

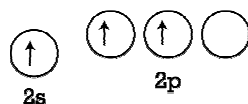
- a. Draw the electron configuration for the central atom before any electron promotion occurs.

Answer:



- b. Draw the electron configuration for the central atom after any electron promotion occurs.

Answer:



- c. Draw the electron configuration after orbital hybridization occurs.

Answer:



7. The formula for beryllium bromide is **BeBr₂**.
 1. Draw the electron configuration for the central atom before any electron promotion occurs.
 2. Draw the electron configuration for the central atom after any electron promotion occurs.
 3. Draw the electron configuration after orbital hybridization occurs.
8. The formula for sulfur hexafluoride is **SF₆**.
 1. Draw the electron configuration for the central atom before any electron promotion occurs.
 2. Draw the electron configuration for the central atom after any electron promotion occurs.
 3. Draw the electron configuration after orbital hybridization occurs.
9. The formula for silicon tetrahydride is **SiH₄**.
 1. Draw the electron configuration for the central atom before any electron promotion occurs.
 2. Draw the electron configuration for the central atom after any electron promotion occurs.
 3. Draw the electron configuration after orbital hybridization occurs.
10. The formula for phosphorus pentaiodide is **PI₅**.
 1. Draw the electron configuration for the central atom before any electron promotion occurs.
 2. Draw the electron configuration for the central atom after any electron promotion occurs.
 3. Draw the electron configuration after orbital hybridization occurs.

The Geometrical Arrangement of Electrons and Molecular Shape

Lesson Objectives

The student will:

- explain the meaning of the acronym VSEPR and state the concept on which it is based.
- state the main postulate in VSEPR theory.
- use VSEPR theory to predict the three-dimensional shapes of simple covalently bonded molecules.
- explain why we treat multiple bonds as if they were single bonds when are determining molecular geometry.
- identify both the electronic and the molecular geometry for simple binary compounds.

Vocabulary

- electronic geometry
- molecular geometry
- unshared electron pair
- VSEPR theory

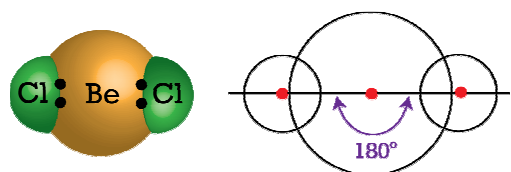
Introduction

Many accurate methods now exist for determining molecular structure, the three-dimensional arrangement of the atoms in a molecule. These methods must be used if precise information about structure is needed. However, it is often useful to be able to predict the approximate structure of a

molecule. A simple model that allows us to do this is called the **valence shell electron pair repulsion (VSEPR) theory**. This model is useful in predicting the geometries of molecules formed by covalent bonding. The main postulate of this theory is that in order to minimize electron-pair repulsion, the electron pairs around the central atom in a molecule will move as far away from each other as possible.

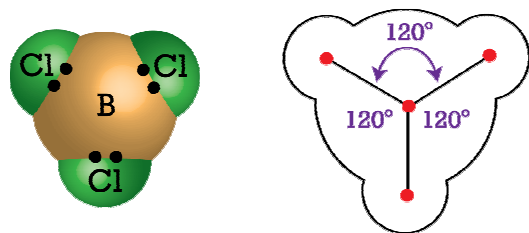
Central Atom with Two Pairs of Electrons

Consider first the covalent compounds formed by Group 2A. An example of such a compound is BeCl_2 . The central beryllium atom has two pairs of electrons in its valence shell. VSEPR theory tells us that these two pairs of electrons will move as far away from each other as possible. The greatest distance that these two pairs of electrons can get between each other is when the two pairs are 180° apart. Since these two pairs of electrons are involved in bonds with the chlorine atoms, the two chlorines will also be on opposite sides of the nucleus. The electronic geometry in this case is *linear*. Since the electron pairs are involved in bonds, the molecule itself will also be linear. As demonstrated in the figure below, a linear molecule means that a straight line would pass through all the nuclei in the molecule.



Central Atom with Three Pairs of Electrons

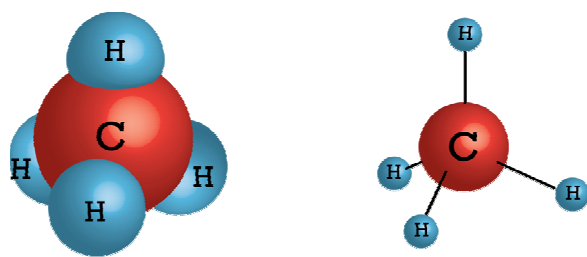
We will look at boron trichloride, BCl_3 , as an example molecule for the covalent molecules in Group 3A. Boron has three valence electrons, with each chlorine that overlaps with a boron orbital contributing one more electron to boron's valence shell. Therefore, boron will have six electrons (three pairs of electrons) in its valence shell. The farthest the three pairs of electrons can move away from each other is to occupy the points of a planar triangle, as illustrated below. Each bond angle will be 120° . This shape is known as *trigonal planar*.



In the trigonal planar shape, all four atoms are in a single plane. None of the atoms project above or below the plane of the paper. You should note that if one pair of electrons is not shared, there will only be two attached chlorine atoms. The shape of such a molecule is called *angular* or *bent*.

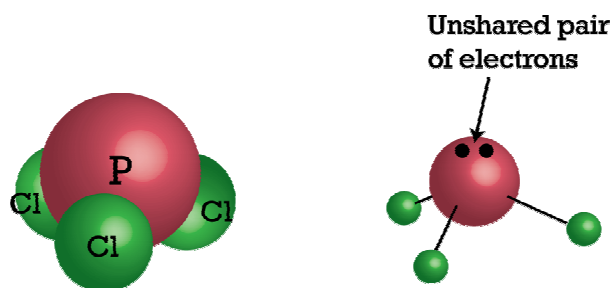
Central Atom with Four Pairs of Electrons

Consider methane, CH_4 , as an example of covalent bonding in Group 4A. Carbon has four valence electrons, with each hydrogen adding one more electron so that the central atom in methane has four pairs of electrons in its valence shell. To maximize the distance between them, the four pairs of electrons form a shape called *tetrahedral*. In the tetrahedral shape, the bond angle between any two hydrogen atoms is 109.5° . If all four pairs of electrons are shared, the molecule shape is also tetrahedral.



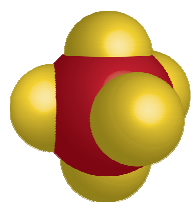
Central Atom with Five Pairs of Electrons

The molecules PCl_3 and PCl_5 will be considered as reference molecules for Group 5A. In the PCl_3 molecule illustrated below, the central phosphorus atom has five valence electrons. Each chlorine atom contributes one more electron, so the central atom has four pairs of electrons in its valence shell. These four pairs of electrons will form the tetrahedral shape in the effort to maximize the distance between them. Therefore, the electronic geometry for this molecule is tetrahedral. When the molecule is formed, however, one of the pairs of electrons is not shared. The resulting molecular geometry is called *pyramidal*.



It is important to note the difference between the pyramidal molecule and the trigonal planar molecule discussed earlier. In the trigonal planar molecule, none of the attached atoms is below or above the plane of the central atom. In this pyramidal molecule, however, all three of the attached atoms are below the plane of the central atom.

In the PCl_5 molecule, the phosphorus has five valence electrons, with each chlorine adding one more. As a result, the central atom will be surrounded by five pairs of electrons in its valence shell. When these five pairs of electrons maximize the distance between them, the shape is called *trigonal bipyramidal*. This shape has three attached atoms in a plane with the central atom and two atoms attached to the two ends of the molecule.

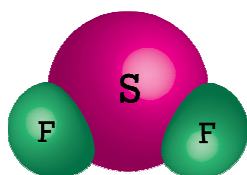


The bond angles between the three atoms in the plane with the central atom are all 120° , while the bond angles between the two end atoms and the other three are 90° .

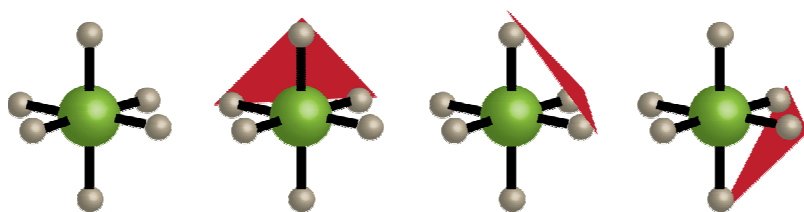
Central Atom with Six Pairs of Electrons

The two types of electronic geometry in Group 6A can be seen in the molecules SF_2 and SF_6 . In SF_2 ,

the central sulfur atom has six valence electrons. Each fluorine adds one more, so the central atom is surrounded by four pairs of electrons. The resultant electronic geometry is the tetrahedral shape we have seen before. However, when the compound SF_2 is formed, two of the pairs of electrons are unshared. This molecular shape, shown below, is called angular or bent.



In the molecule SF_6 , sulfur has six valence electrons, with each fluorine contributing another electron so that the central atom is surrounded by six pairs of electrons. The maximum distance six pairs of electrons can separate produces an electronic geometry called *octahedral*.



The bond angle between any two adjacent attached atoms is 90° . The shape name is based on the number of triangular plates that can be placed on the surface of the molecule, as illustrated above. If you count carefully, you will see that the surface of the molecule contains eight triangular plates, hence the name octahedral.

Table [below](#) summarizes the electronic geometries that have been presented so far in this chapter.

Summary of Electronic Geometry

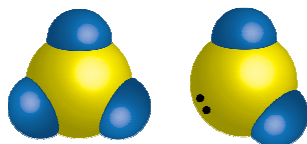
Electron Pairs	Hybridization	Electronic Geometry
1	None	Linear
2	sp	Linear
3	sp^2	Trigonal Planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal Bipyramidal
6	sp^3d^2	Octahedral

Examples of Molecular Shapes

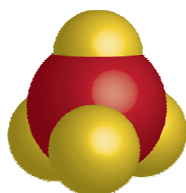
The electronic geometry for a given number of electron pairs surrounding a central atom is always the same. Electron pairs will distribute themselves in the same way to maximize their separation. The same thing cannot be said for molecular geometry. The molecular shape depends on not only the electronic geometry, but also the number of the shared electron pairs. In this section, we will consider a number of examples where some of the electron pairs are not shared.

There are only a few possible molecular geometries available to the members of Group 3A. Consider the shapes of the BH_3 molecule and the BH_2^- ion. In BH_3 molecules, the central atom is surrounded by three pairs of electrons, so the electronic geometry is trigonal planar. When all three electron pairs are

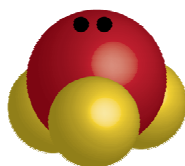
shared, the molecular geometry is also trigonal planar, as shown on the left in the diagram below. For the BH_2^- ion, there are still three pairs of electrons around the central atom (3 electrons come from boron, 1 from each of the two hydrogens, and 1 from outside the ion), so the electronic geometry is still trigonal planar. The shape of the ion, however, will be a shape known as bent or angular, as shown on the right in the diagram below.



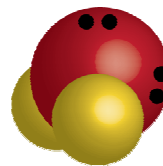
When the central atom is surrounded by four pairs of electrons, the electronic geometry will always be tetrahedral. When all four electron pairs are shared, like in the molecule CH_4 , the molecular shape will also be tetrahedral. In the case of ammonia, NH_3 , only three of the four pairs of electrons are shared. This results in a molecular shape called pyramidal. If a second pair of electrons is unshared, which is the case for H_2O , the shape is angular again. The possible molecular geometries for molecules where the central atom is surrounded by four pairs of electrons are illustrated below.



Electronic Geometry: Tetrahedral
All electron pairs shared.
Molecular Geometry: Tetrahedral

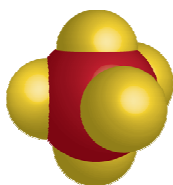


Electronic Geometry: Tetrahedral
One unshared pair of electrons.
Molecular Geometry: Pyramidal



Electronic Geometry: Tetrahedral
Two unshared pairs of electrons.
Molecular Geometry: Angular (bent)

When the central atom is surrounded by five pairs of electrons, the electronic geometry is trigonal bipyramidal. If all the electron pairs are shared, the molecular geometry will also be trigonal bipyramidal. An example of such a molecule is PF_5 . If one pair of electrons is not shared, the molecular shape is a *distorted tetrahedron*, which is sometimes called *seesaw*. An example of a molecule with trigonal bipyramidal electronic geometry and a distorted tetrahedron molecular shape is SF_4 . When the electronic geometry is trigonal bipyramidal and two pairs of electrons are unshared, the shape is *T-shaped*. An example of a T-shaped molecule is ClF_3 . ClF_3 has five pairs of electrons around the central atom, but only three of them are shared. When only two electron pairs in the trigonal bipyramidal electronic geometry are shared, the molecular geometry produced is linear, which is the case for I_3^- . The trigonal bipyramidal, distorted tetrahedron, T-shaped, and linear molecular structures are shown in the diagram below.



Electronic Geometry: Trigonal Bipyramidal
All electron pairs shared.
Molecular Geometry: Trigonal Bipyramidal



Electronic Geometry: Trigonal Bipyramidal
One unshared pair of electrons.
Molecular Geometry: Distorted Tetrahedron

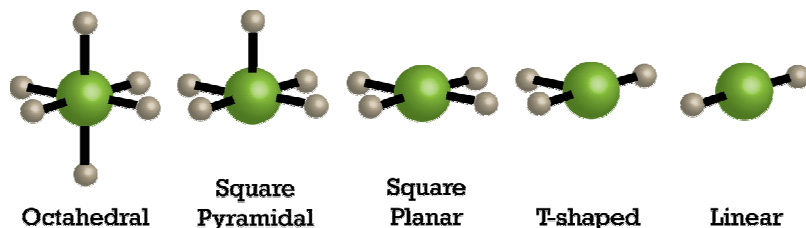


Electronic Geometry: Trigonal Bipyramidal
Two unshared pairs of electrons.
Molecular Geometry: T-shaped



Electronic Geometry: Trigonal Bipyramidal
Three unshared pairs of electrons.
Molecular Geometry: Linear

Beginning with octahedral electronic geometry (six pairs of electrons), a number of molecular shapes can be produced depending on the number of electron pairs that are shared and unshared (see the illustration below).



For a trigonal bipyramidal electronic geometry, unshared electron pairs prefer to be in the equatorial positions (the points of the triangle in the “trigonal” plane). For an octahedral electronic geometry, unshared electron pairs prefer to be on opposite sides of the molecule. These rules help rule out other molecular shapes that could potentially occur when dealing with central atoms surrounded by five or six electron pairs.

Table [below](#) summarizes the different molecular geometries.

Summary of Molecular Geometry

Valence Shell Electron Pairs Total	Valence Shell Electron Pairs Shared	Valence Shell Electron Pairs Unshared	Molecular Geometry
1	1	0	Linear
2	2	0	Linear
2	1	1	Linear
3	3	0	Trigonal Planar
3	2	1	Angular
3	1	2	Linear
4	4	0	Tetrahedral
4	3	1	Trigonal Pyramidal

4	2	2	Angular
4	1	3	Linear
5	5	0	Trigonal Bipyramidal
5	4	1	Distorted Tetrahedron
5	3	2	T-shaped
5	2	3	Linear
5	1	4	Linear
6	6	0	Octahedral
6	5	1	Square Pyramidal
6	4	2	Square Planar
6	3	3	T-shaped
6	2	4	Linear
6	1	5	Linear

An animation showing the molecular shapes that are generated by sharing various numbers of electron pairs around the central atom (includes shapes when some pairs of electrons are non-shared pairs).

The Effect of Pi Bonds

For the process of predicting electronic or molecular geometry, double bonds and triple bonds should be counted as one effective pair when determining the number of electron pairs around the central atom. In order to repel other electron pairs, the electron pairs must be placed between the nuclei of two atoms. In pi bonds, the electron density is above and below the plane of the bond and therefore does not contribute to electron pair repulsion. *For the VSEPR model, multiple bonds count as only one effective pair of electrons.* We can use the nitrate ion, NO_3^- , seen below as an example. In order to determine the shape of the nitrate ion, we count the number of electron pairs that are surrounding the central nitrogen atom. Since double bonds count as a single electron pair for the VSEPR model, we would count three pairs of electrons in the central atom's valence shell, and the shape of the ion would be trigonal planar.



Examples of Determining Molecular Geometry

Example:

Determine the shape of the ammonium ion, NH_4^+ .

Solution:

First determine the number of electron pairs around the central nitrogen atom.

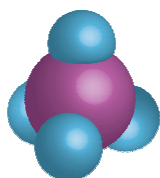
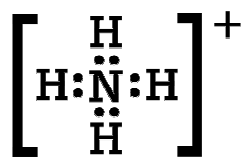
Electrons = 5 (from nitrogen) + 4 (one from each hydrogen) - 1 (the positive charge on the ion indicates this ion has lost one electron to the outside) = 8 electrons = 4 electron pairs

The next step is to choose the electronic geometry based on the number of electron pairs.

The electronic geometry of a central atom with four pairs of electrons = tetrahedral.

Finally, choose the molecular geometry based on the number of valence shell electron pairs that are shared and not shared.

Since all four pairs of electrons are shared in this ion, the ionic shape will be tetrahedral, as seen below.



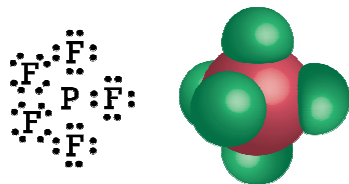
Example:

Determine the molecular shape of the PF_5 molecule.

Solution:

Electrons in the valence shell of phosphorus = 5 (phosphorus) + 5 (one from each fluorine) = 10 electrons = 5 pairs of electrons.

The electronic geometry is trigonal bipyramidal. Because all five pairs of electrons are shared, the molecular geometry will also be trigonal bipyramidal, illustrated below.



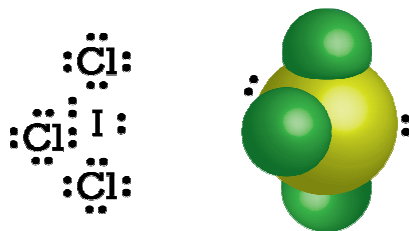
Example:

Determine the shape of the ICl_3 molecule.

Solution:

The number of electrons surrounding the central iodine atom 10: 7 electrons come from the iodine atom, and 1 electron comes from each chlorine atom. As a result, there are 10 electrons, or 5 electron pairs, surrounding the central iodine atom. Therefore, the electronic geometry is trigonal bipyramidal. Since

only three of the electron pairs are shared, the molecular geometry is T-shaped.



Example:

Determine the shape of the CO_2 molecule.

Solution:

Since there are multiple bonds involved in this molecule, we need to write the Lewis structure for the molecule to make sure we do not count any double or triple bonds for VSEPR model determinations. The Lewis structure for CO_2 is shown below.



Only the sigma bonds count in determining the electron pairs surrounding the central carbon atom. This molecule, therefore, has two electron pairs in the valence shell of the central atom, which produces linear electronic geometry. Since both pairs are shared, the molecular geometry will also be linear.

Example:

Determine the shape of the SO_2 molecule.

Solution:

We will write the Lewis structure (shown below) to check for multiple bonds.



In writing the Lewis structure for SO_2 , we determined that a double bond is necessary to provide an octet of electrons for the central sulfur atom. Therefore, this molecule has three pairs of electrons around the central atom, so its electronic geometry will be trigonal planar. Since only two of the electron pairs are shared, the molecular geometry is angular.

Example 6:

Determine the molecular shape of the XeF_4 molecule.

Solution:

The number of electrons surrounding the central atom in XeF_4 is twelve: eight electrons from the Xe,

and one each from the four fluorine atoms. As a result, there are twelve electrons, or six electron pairs, around the central atom Xe. Six pairs of electrons around the central atom produces an octahedral electronic geometry. Since two pairs are unshared, the molecular geometry will be square planar.

Lesson Summary

- VSEPR theory suggests that the valence shell electron pairs will spread themselves around the central atom in an attempt to maximize the distance between them due to electrostatic repulsion.
- The electronic geometry of a molecule is dependent only on the number of electron pairs in the valence shell of the central atom.
- Molecular geometry is dependent on the electronic geometry and on the number of electron pairs that are unshared.
- Electrons in pi bonds do not contribute to electronic and molecular geometry.

Further Reading / Supplemental Links

The *learner.org* website allows users to view the Annenberg series of chemistry videos. You are required to register before you can watch the videos, but there is no charge to register. The video called “Molecular Architecture” is related to this lesson.

- <http://learner.org/resources/series61.html>

This website reviews how to predict molecular structure by using the VSEPR theory.

- http://www.up.ac.za/academic/chem/mol_geom/mol_geometry.htm

This video is a ChemStudy film called “Shapes and Polarities of Molecules.”

- <http://www.youtube.com/watch?v=BnU2idxQ3Xc>

Review Questions

1. What is the designation for the hybrid orbitals formed from each of the following combinations of atomic orbitals in **Table below**, and what is the bond angle associated with the hybrid orbitals?

Table for Review Question 1

Orbitals Combined Type of Hybridization Bond Angles

one *s* and one *p*

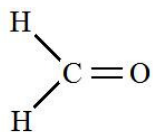
one *s* and two *p*

one *s* and three *p*

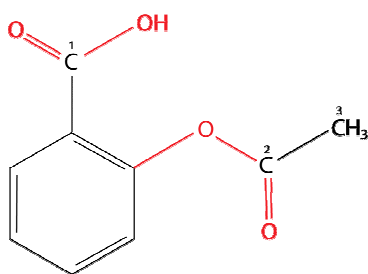
2. Draw a Lewis structure for OF_2 that obeys the octet rule.
3. Draw a Lewis structure for H_2CO that obeys the octet rule. (C is the central atom.) What is the geometrical shape of this molecule?
4. What is the bond angle in SCl_2 ?
5. What is the molecular shape of ICl_3 ?
6. What is the molecular shape of XeCl_4 ?
7. The ion I_3^- molecule has been produced in the lab, but the ion F_3^- has not. Offer an explanation as

to why F_3^- cannot be produced in the lab.

8. The molecule shown here is formaldehyde. What is the hybridization of the carbon atom in this molecule?



1. sp^2
 2. sp^2d
 3. sp^3
 4. 5 pi bonds
9. The molecule shown here is acetylsalicylic acid, better known as aspirin.



1. What is the hybridization of carbon 1?
2. What is the hybridization of carbon 2?
3. What is the hybridization of carbon 3?
4. What is the total number of pi bonds in the molecule?

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